

309
W67

WILLIAMS

Artificial silicates

Chemistry

B. S.

1909

UNIVERSITY OF ILLINOIS
LIBRARY

Class

1909

Book

W67

Volume

Mr10-20M





Digitized by the Internet Archive
in 2014

<http://archive.org/details/artificialsilica00will>

ARTIFICIAL SILICATES

~~826~~
243944

BY

WARREN STEPHEN WILLIAMS

THESIS FOR THE DEGREE OF BACHELOR OF SCIENCE

IN CHEMISTRY

IN THE

COLLEGE OF SCIENCE

OF THE

UNIVERSITY OF ILLINOIS

Presented June, 1909 *w*

UNIVERSITY OF ILLINOIS

June 1st 1909

This is to certify that the thesis prepared
under my supervision

by W. S. Williams

entitled Artificial Silicates

is approved by me as fulfilling this part of
the requirement for the

degree of Bachelor of Science

in Chemistry

Swann

Instructor in Charge

Approved W. A. Noyes

Head of Department of Chemistry

168145

23N10 Craig

ARTIFICIAL SILICATES WITH REFERENCE TO AMORPHOUS SILICA.

(By W. S. WILLIAMS.)

CONTENTS.

	Page.
Introduction	277
General	277
Acknowledgments	278
Scope of this work	278
Development of the sand—lime brick process	278
Sand-brick with exclusive carbonate filler	279
Sand-brick with carbonate and silicate filler	279
Sand-brick with hydrosilicate filler	279
Wet slaking process	280
The dry slaking process	280
The acid slaking process	280
The quick lime process	281
Description	281
Mixing	281
Pressing and hardening	281
Experimental work	282
Conditions of the experiments	282
The proper ratio of lime to silica to form the strongest bond	282
Effect of adding fibrous materials	284
Effect of sharp sand	286
Superheated steam	287
Fire tests	287
Carbonate filler versus silicate bond	289
The effect of using dolomite as a substitute for lime	290
Silica and orthoclase	290
A substitute for clay-products	291
Conclusions	291
Bibliography	292

INTRODUCTION.¹

GENERAL.

In southern Illinois there are large deposits of amorphous silica which have been worked but little. This fine grained, white, substance is used as a filler for wood, for paints, for scouring soaps, toilet powders, porcelain bodies and glazes. These deposits are being worked by several firms at present, practically all of the mining being done by hand. The preparation consists of fine crushing and of careful sizing of the material. The supply far exceeds the demand and the effect of opening these recently discovered deposits has been to overstock the market and lower the price of amorphous silica.

The geology of this region is not very well known. Mr. F. W. DeWolf visited this territory in 1906 in the interests of the State Geological Survey and made preliminary observations on the geological formation and also collected samples. He states that the material occurs as bedded deposits, varying in thickness from a few feet to six or eight feet. A preliminary report is found in Bulletin No. 4 of the Illinois State Geological Survey. The following table shows the chemical analyses of the samples collected, as reported in the above mentioned bulletin:

TABLE No. 1.

Number.	SiO ₂ .	Per cent		Loss on Ignition.
		Fe ₂ O ₃	Al ₂ O ₃	
203.....	87.90	3.72		2.84
204.....	82.26	6.04		1.76
205.....	95.14	2.38	
206.....	90.24	5.88	
207.....	95.18	1.04	
208.....	90.04	2.36	
209 ²	73.78	14.56		5.43
210.....	97.20	1.28	
211.....	93.78	1.80	
212 ²	77.82	10.26	

¹ Presented as a thesis to the faculty of the University of Illinois for the degree of B. S. in chemistry. The work was done under the direction of Prof. S. W. Parr, on whose suggestion it is included in this Year Book.

²NOTE—Iron and alumina were separated in 209 and 121.

ACKNOWLEDGMENTS.

Acknowledgment is due to Mr. C. F. Hagedorn, a graduate of the University of Illinois in 1905, who in the fall of that year began a line of research in an attempt to make siliceous bricks; and to Mr. C. H. McClure, who subsequently took up the work and made a few determinations of lime and silica. Neither of these men carried this particular work further. Mr. H. B. Fox, in tests on sand-lime brick, used the samples made by the above men. The next person to take up this interesting work, was Mr. T. R. Ernest, working under the direction of Prof. S. W. Parr, in the laboratory of Applied Chemistry, of the University of Illinois. He had three objects in view in his investigation, viz.:

1. To study the sand-lime brick process, including a review of the literature and experiments.

2. To study the compound formed by the action of high pressure steam on mixtures of lime and silica, from both the chemical and physical standpoint.

3. To find uses for Illinois silica.

In this thesis, Mr. Ernest shows that the chemical compound formed by the action of high pressure steam on intimate mixtures of lime, and silica is probably the mono-hydro calcium silicate which may be considered analogous to the meta silicate Wollastonite (Ca O, Si O_2), with one molecule of H_2O of hydration. He also states that the best proportions in mixing are equal parts of lime and silica. In running fire tests on this mixture he did not measure the temperatures but found that the mixture cracked badly in a suddenly heated muffle furnace.

SCOPE OF THIS WORK.

The object of these investigations is to determine by means of the tensile strength:

1. The proper ratio of lime to silica to form the strongest bond.

2. To improve the texture of the mixture by suction, boiling and using plaster of Paris molds.

3. To increase the strength of the mixture by adding fibrous materials thereto.

4. To determine whether the material can be molded into shapes which would be useful for architectural decoration.

5. To determine the effect of fire on this material.

6. To determine whether steam pressure is necessary and, if so, what pressure is most suitable to give the strongest bond.

DEVELOPMENT OF THE SAND-LIME BRICK PROCESS.

It is a well established fact that a moist mixture of sand and slaked lime becomes hard on being exposed to the air, a process which depends upon the absorption of carbon dioxide. For many years "mortar-brick" have been made, dependent on this reaction. It forms calcium carbonate, which acts as the cementing material. The making of sand-lime brick with calcium silicate as a filler does not date back more than thirty years. In this a chemical combination takes place between the two constituents, slaked lime and sand, which binds the two together in a manner similar to vitrification.

SAND-BRICK WITH EXCLUSIVE CARBONATE FILLER.

It is readily understood that a stone with calcium carbonate as a filler is not as strong as one with a calcium silicate union.¹ Twenty to 40 per cent of completely slaked lime is added to sand and thoroughly mixed with sufficient water to allow easy molding. This is then hardened by one of three methods:

1. The brick is exposed to the atmosphere for a long time,² the caustic lime thus slowly acquiring the needed carbon dioxide $\text{Ca(OH)}_2 + \text{CO}_2 = \text{CaCO}_3 + \text{H}_2\text{O}$. The necessity for complete slaking is quite evident since any unslaked lime would slake later and rupture the brick. The time required before use is five or six months, and a maximum strength is attained in one or two years. The hardening is similar to that of mortar and is only superficial. Zurick says that only 30 per cent of the lime in very old mortars has been converted into the carbonate.

2. Hardening in an atmosphere rich in carbon dioxide without pressure. This gives the same results as the first process but in much shorter time.

3. Hardening with carbon dioxide under pressure. For this process the advantage is claimed that nearly all of the Ca(OH)_2 is converted into carbonate. However, Prof. Rinne of Hanover does not believe that this is satisfactorily proven and he is of the opinion that the carbon dioxide will form a carbonate on the surface, closing the pores of the brick, and thus preventing the entrance of enough carbon dioxide into the body of the brick to make the conversion to the carbonate complete.

SAND-BRICK WITH CARBONATE AND SILICATE FILLER.

In this process the treatment up to the hardening point is the same as that just described but the hardening is effected in a warm moist atmosphere, saturated with CO_2 . A combination of these methods provides for the introduction of CO_2 into kettles or closed iron cylinders used for steam hardening. Under the conditions first cited, the product has as a binding material for the most part CaCO_3 , but some hydrated calcium silicate is probably formed, thus strengthening the bond. In the latter the binding material is mainly calcium hydrosilicate and the amount of carbonate is much less than in the former.³

SAND-BRICK WITH HYDROSILICATE FILLER.

This brings us to the third class, the only one which will ever be of any importance in the commercial world. The same raw materials are used as in the other process, viz.: sand and lime. The subsequent paragraphs will be devoted to a review of the literature on this subject.

In present practice⁴ one of four methods prior to hardening are employed, the different features being the method of preparing the lime:

1. Wet slaking process.
2. Dry slaking process.
3. Acid slaking process.
4. Quick lime process.

¹See bibliography, 16.²See bibliography, 1.³See bibliography, 13.⁴See bibliography, 3.

THE WET SLAKING PROCESS.

This process consists in slaking the lime to a fat putty and then mixing in the desired proportion of sand and water.¹ From this it is carried to bins over the press and allowed to stand a short time and then pressed.

With properly burnt high calcium lime, the addition of the proper amount of water can be made with enough labor. The heat given up by the union of caustic lime and water is sufficient to generate steam in the minute pores of the amorphous oxide and thus break it up into the smallest possible particles, constantly and rapidly exposing new surfaces to the hot water. Calcium oxide on hydration gives up 246 calories of heat per gram. Under these conditions the CaO seems to form a hydrate, carrying more than one molecule of water. The excess is locked so loosely that a little excess of heat, as would be the case with too little water, would prevent its formation. If there is insufficient water, the lime will become too hot, or be too dense, for the best results. The product of correct slaking is an extremely tough and plastic mass.

Walters found that the best slaking of high calcium lime gave an increase of 3.5 times the original volume, while air slaking gave 2.5 times, and slaking with a large quantity of water 1.7 times the volume. The increase in volume gives better spreading or enveloping power.

With the dolomites,² more time is required for proper slaking for the two following reasons:

1. The magnesium oxide is overburned at the temperature of complete expulsion of carbon dioxide from limestone and is hence above its point of maximum porosity.

2. The heat evolved by magnesium oxide on hydration is much less than that for the hydration of CaO. The presence of both acts in the direction of retardation. Pure dolomite lime yields 130 calories of heat per gram.

If this process is used it will be found advantageous to mix the lime into a cream which will favor its even distribution over the sand grains.

THE DRY-SLAKING PROCESS.

This differs from the preceding only in the fact that the lime is slaked with just enough water so that the heat of chemical reaction will dry the finished hydrate.³ The hydration is incomplete in most cases. For sand-lime brick a steam-slaked lime is always safe, since the lime has reached the limit of expansion under the action of steam. Where magnesium lime is used this is the method which should be used because the dolomitic limes slake too slowly for any other process.

The fine state of division in which the lime hydrate is left after dry-slaking gives it the best possible physical condition for uniform distribution and chemical reaction. The dry hydrate can be rapidly and also completely incorporated into the sand and when water is later added there is but slight tendency to ball up.

THE ACID-SLAKING PROCESS.

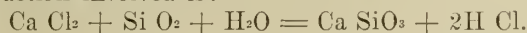
In this process 5 to 10 per cent of a solution of hydrochloric acid, 19° Baumé, is added to the lime after slaking has begun.⁴ This is the basis of a German patent issued to P. Kleber. In the preliminary slaking the

¹See bibliography, 27. ²See bibliography, 28. ³See bibliography, 5, 27. ⁴See bibliography, 8.

hydration is carried only from one-third to one-fifth of completion, so that only one-third or one-fifth of the lime is changed into calcium chloride.

This compound, as is well known, has a great affinity for water and is also very active in attacking silicates as is illustrated by its action in the nascent condition made use of in the J. Lawrence Smith method for the determination of the alkakies.

The introduction of calcium chloride would be objectionable since, if the chloride remains as such, it would later appear as an efflorescence because of its solubility. If it is decomposed, and calcium silicate formed, the acid liberated in the atmosphere of steam must surely attack the metal cylinders unless they are glazed or lined with lead. The reaction involved is:



THE QUICK-LIME PROCESS.

Description.—In this the dry calcium oxide is mixed with the sand and just enough water added to slake the lime.¹ The water is generally added in two portions, with a short interval between additions to give the lime time to absorb all the water possible. The production then goes to the press, but should not reach it until at least twenty minutes have elapsed, in order to give the lime time to slake. This appears to be the most rational and rapid method where the materials are available. There is no rehandling of any of the materials. The sand and lime start in together at one end of the plant and come out at the other a finished product without intermediate delay. This method is not adapted to the use of all kinds of limes, for it requires a sensitive, quick-slaking lime and one which therefore has not been overburned nor stored for any length of time. A sand containing considerable moisture can be used without disadvantage, since the absorption of water by the quick-lime will remove considerable moisture from the sand and the heat generated by slaking will aid evaporation. If the plant is properly arranged, the mixture will go through the press while still warm and into the hardening cylinder before cold. In this manner some steam is saved in the hardening process, since not quite so much steam is condensed in raising the temperature of the brick up to the temperature of the steam. The amount of steam condensed will, of course, be proportionately less, the higher the initial temperature of the brick.

Mixing.—The key to the success of the process lies in the thorough mixing of the constituents, and for this purpose nearly every known mixing device has been used.² The ones most extensively used today are: the Schwarz mixer, the pug mill, and the tube mill.

Pressing and Hardening.—In view of the nonplastic nature of the mixtures they do not flow evenly through a die, hence they cannot be used with a clay-brick machine. On the other hand, a dry-press for clay-brick must be greatly strengthened, in order to stand high pressures. After trials of all the various kinds of presses, the rotating table press predominates in Europe, while in America the preference is divided between the table-press and the upright dry-press.

¹See bibliography, 13.

²See bibliography, 14.

The hardening is accomplished by one or two methods, either by low pressure steam and long exposure, or high pressure steam and short exposure. In the former case about two atmospheres are used for seventy-two hours, giving a temperature of 125°C , and in the latter from seven to ten atmospheres for six to ten hours are used, giving a temperature of 170 to 185°C . This last is now universally used in the industry.

EXPERIMENTAL WORK.

CONDITIONS OF THE EXPERIMENTS.

Test briquets were made in a standard cement briquet mold, using amorphous silica from southern Illinois and lime of a good commercial quality, which was slaked in the steam autoclave before adding to the silica. The batches were weighed on a scale sensitive to one-tenth of a gram. Then the ingredients of a batch were put into a dry ball mill and ground for at least two hours to insure perfect blending and homogeneity. After removal from the mill, the mixture was screened through a fifty-mesh sieve, mixed with water and then immediately molded into briquets. The amount of water used was sufficient to make the mixtures work well. The mixture of lime and silica was found to be nearly as plastic as Georgia kaolin. The amount of water necessary to gain this plastic state was found to be 250 cubic centimeters added to 500 grams of the mixture. By volume, this would be two parts mixture to one part of water. This amount was used throughout the experiments.

If the briquets were allowed to dry too rapidly, they checked badly on the drying surface. This was overcome by placing damp cloths over them. By this procedure the capillary system of the drying surface is kept open until the interstitial water of the interior of the briquet has dried out. Then the cloths were removed and the capillaries of the surface allowed to dry and close up. It was also discovered that if the briquets were too wet when steamed they would crack open and fall apart. This is due to the water of capillarity being converted into steam which, having no ready egress, bursts the form. Taking the above mentioned facts into consideration, it was determined to let the briquets dry for at least thirty-six hours before steaming them. This was adhered to during the course of this work. However, it must be understood that, if the unsteamed briquets are exposed to the air for too long periods of time, the carbon-dioxide of the air will react with part of the calcium hydrate to form the carbonate and thus the ultimate strength will be reduced.

After the briquets were steamed they were dried, and aged for a week. They were then tested for tensile strength on a standard Fairbank's automatic machine, such as is used in testing cement.

THE PROPER RATIO OF LIME TO SILICA TO FORM THE STRONGEST BOND.

Naturally the first consideration is to determine the effect of various per cents of lime and silica on the tensile strength: and, also, what proportion gives the highest tensile strength, or, in other words, the strong-

est bond. Accordingly, briquets were made up of different percentages of lime and hardened in the autoclave. Table II below shows the relations of lime to silica used and the results:

TABLE II.

Data:—Steam pressure, 105 lbs. per square inch. Time exposed to steam, 10 hours.

Per Cent Ca O.	Per Cent SiO ₂	Tensile strength in lbs. per sq. in.
10.....	90	135
20.....	80	265
30.....	70	202
40.....	60	189
50.....	50	150

Table III illustrates the increase in tensile strength when a higher steam pressure is used:

TABLE III.

Data:—Steam pressure, 150 lbs per square inch. Time exposed, 10 hours.

Per Cent Ca O.	Per Cent SiO ₂	Tensile strength in lbs. per sq. in.
10.....	90	134
20.....	80	278
30.....	70	204
40.....	60	189
50.....	50	148

In Table IV is shown the decrease in tensile strength when a low steam pressure is applied:

TABLE IV.

Data:—Steam pressure, 50 lbs. per square inch. Time exposed, 10 hours.

Per Cent Ca O.	Per Cent SiO ₂ .	Tensile strength in lbs. per sq. in.
10.....	90	102
20.....	80	182
30.....	70	116
40.....	60	94
50.....	50	71

All of the above data are the averages of five or more tests. It is easily seen that the strength increases remarkably with the increase in the lime content, until twenty per cent of lime is reached, and then

falls almost as rapidly as it increased, when more than twenty per cent of lime is added. The tensile strength does not increase in the same proportion between 105 pounds pressure, as it does between 50 and 105 pounds pressure. These results were all verified by running tests in which the lime content varied by only three per cent instead of ten as given in the tables, and when the maximum point was approached the ratio of lime to silica were varied by only one per cent. The texture of the broken briquets was an open structure with frequent air holes. Assuming that this open structure could be eliminated and a more compact body formed, tests were run by the following methods:

(1) By mixing the constituents with sufficient water to form a cream and then exhausting the air from it. The creamy mass was then carefully poured into the molds so that no air was occluded.

(2) By boiling the air out of the creamy mass and proceeding as above mentioned.

(3) By pouring the viscous mixture into molds made of plaster of Paris.

Although many trials were made, the results were unsatisfactory. The averages of the trials made by the first method is only 213 pounds per square inch as against 278 pounds found in Table III. The second method yielded even poorer results, being 204 pounds per square inch. But the third method gave the best results, the average reaching 226 pounds per square inch. The failure of these methods to increase the tensile strength of the 20 per cent lime to 80 per cent silica mixture, hardened at 150 pounds per square inch, and exposed for 10 hours, is probably due to several causes. First, in none of the methods could pressure be applied while molding the briquet; second, in methods 1 and 3, the silica having a higher specific gravity than the lime, tended to settle out of the fluid while in the mold; third, while what has just been said above applies equally well to method 2, it is also very probable that the heat tended to start the chemical reaction between the lime and silica, and that this reaction was stopped by the molding period and hence the bond was weaker.

The texture of these briquets was very good with respect to the air bubbles contained and the compact nature of the body:

EFFECT OF ADDING FIBROUS MATERIALS.

Mineral wool, otherwise known as slag wool, was the first fibrous material added to the 20 per cent lime mixture. A series was run ranging from 2 per cent to 10 per cent of wool added. This did not increase nor decrease the strength but seemed to act as an inert substance.

The other substance investigated, having a fibrous stringy nature, which would be commercially feasible, was cheap asbestos threads. The increase in strength was quite marked and is illustrated in Table V.

TABLE V.

Data:—Steam pressure, 150 lbs. per square inch. Time exposed, 10 hours.

Per Cent of Asbestos Added.	Tensile strength in lbs per sq. in.	Increase in strength in lbs. per sq. in.
3.....	285	7
4.....	297	19
5.....	300	22
10.....	343	65
12.....	377	100
14.....	302	24
20.....	242	36 decrease.
40.....	173	105 decrease.

From this table it will be observed that the increase in tensile strength rises gradually, until, when twelve per cent of asbestos is reached it drops suddenly. This shows that after twelve per cent is passed, the mixture is overburdened, and the asbestos acts as a retarder to the chemical reaction between the lime and the silica.

The effect of adding colloids was next determined by mixing into the 20 per cent lime mixture, sodium silicate, ($\text{Na}_2\text{O SiO}_2$), also called soluble glass, and Portland cement. Both of these substances decreased the strength of the briquets in the direct proportion in which they were added. This fact is easily seen from Tables VI and VII.

TABLE VI.

Data:—Steam pressure, 150 lbs. per square inch. Time exposed, 10 hours.

Per Cent $\text{Na}_2\text{O SiO}_2$ Added.	Tensile strength.	Decrease in strength.
1.....	189	101
2.....	175	105
4.....	114	166
5.....	82	198
10.....	50	230

TABLE VII.

Data:—Steam pressure, 150 lbs. per square inch. Time exposed, 10 hours.

Per Cent Portland Cement Added.	Tensile strength.	Decrease in strength.
2.....	97	183
5.....	93	187
10.....	55	125

The resultant decrease shown in Table VI is probably due, in part, to the fact that the sodium silicate was broken up by some of the dis-

solved calcium hydrate. However, in both cases the reduced strength may be explained by assuming that the grains of the mixture were kept apart by the colloidal substances.

EFFECT OF SHARP SAND.

The influence of inert substances as reviewed above suggested the use of materials which would not be of a colloidal nature. Sharp, ground, quartz, sand was added. The results are tabulated in Table VII.

TABLE VII.

Parts sand added to 100 parts standard mixture.	Tensile strength	Decrease in strength.
2.....	76	202
5.....	50	228
10.....	106	172
20.....	119	159
30.....	124	154
40.....	160	118
50.....	179	98
60.....	205	73
70.....	219	59
80.....	243	35
90.....	172	106
100.....	116	162

An inspection of the above table shows that the introduction of sharp sand decreases the total strength and, it may be added, results in a coarse porous body. For particular purposes, where such a body may be demanded, it is readily seen that eighty parts of sand yields the best results. However, in the use of this body the increase in the ratio of voids over the silica body must be considered. This would, of course, be an advantage where heat conductivity was the primary qualification, but a disadvantage with respect to weathering.¹ Slichter in discussing the origin and relations of pore-space in sands and sandstones, has shown that it depends upon the size of grains, their uniformity of size, and the manner in which they are packed.² Therefore, by adding the fine amorphous silica to regular sand-lime brick mixture, the expensive grinding of a part of the quartz and sand as carried out by the majority of manufacturers could be avoided. This would very materially reduce the cost. On the other hand, if a body could be used of eighty parts sand in place of the pure silica body, the cost of the product would be greatly reduced because sand is not as expensive as the amorphous silica.

¹ See bibliography, 29.

² See bibliography, 30.

SUPERHEATED STEAM.

The question naturally arises as to whether the chemical combination is produced by the higher temperature of steam under pressure or by the united effect of pressure and temperature. In order to investigate this question, an apparatus was arranged, consisting of a covered iron container for the briquets into which super-heated steam was introduced but which had ready egress into the air. Thermometers were placed in the steam jet and in the container for reading the temperatures. No steam pressure was used in the container. Although temperatures were used ranging from 175° centigrade up to 430° centigrade, and the time of exposure ranged from ten to forty-eight hours, no reaction could be obtained.

For this experiment new briquets were introduced into the container for each test. This was done in order to avoid the possible building up and destruction of the chemical bond, which might form. Repeated attempts to chemically combine the silica and lime by this means ended in failure. Hence, it would seem to be conclusively shown that, steam under pressure is absolutely essential to the successful bonding of lime and silica.

FIRE TESTS.

One of the main considerations taken into account when a building material is being examined is its action under fire. Accordingly fire tests were made on briquets of 20 per cent lime to 80 per cent silica in composition. These tests were made in a muffle furnace and also in a test kiln in direct contact with the fire gases. It was found that if the briquets were heated suddenly to a temperature of 800° C., which is a red heat, they cracked and burst open, at times with sufficient force to scatter the pieces a foot or so away. In these cases 800° C. was reached in twenty or thirty minutes. On the other hand, if 800° temperature was gained in from forty-five to sixty minutes, the briquets were sound and no evidence of cracking could be observed. The fact that the suddenly heated trials burst the briquets is probably due to the fact that the outer surface of the briquets were fritted before the water in the interior had time to volatilize. This explanation is more readily understood when it is considered that the chemical formula of this silicate has been shown¹ to be CaO , SiO_2 , H_2O . The water, as has been said before, is chemically combined and hence does not readily break away from the other constituents, but it does detach itself at the higher temperatures. If these are quickly reached, the surface is slagged over and the water is converted to steam, which, having no ready egress, will burst the briquet. In order to determine the effect of heat on the chemical bond, trial pieces were placed in the furnace and drawn at regular temperature intervals. The heating was done over a comparatively long period of time, three hours, so that the danger from sudden heating might be avoided. The results are set forth in Table VIII.

¹See bibliography, 33.

TABLE VIII.

Test No.	Drawn at temperature degrees C.	Tensile strength.
1.....	300	45
2.....	400	0
3.....	500	101
4.....	600	131
5.....	700	124
6.....	750	27
7.....	800	71
8.....	850	186
9.....	1190	260
10.....	1390	263

The results here recorded reveal some startling effects, for instance, at 400° C., the tensile strength drops to zero, then at 600° C. there is shown a maximum point after which there is again a sharp fall to a tensile strength of 27 pounds at 750° C. After this temperature is past, the bond is strengthened rather gradually until 1190° is reached, when it is practically at its maximum strength, for at 1390° the strength was only three pounds more. Higher temperatures than this were not attained. These results are very puzzling and although they were checked by two other similar tests, more work along this line should be done before any definite statements can be made. The peculiar action of this bond under fire might be explained by analogy. For example, in the burning of clay wares the greater percentage of mechanical water is expelled by the time 400° C. is reached, leaving the body weak and friable. At 750° the clay body begins to increase in strength until it reaches the maximum. When 750° is attained practically all of the chemically combined water is eliminated. This is also probably the case here. But just why the loss of mechanical water should allow an increase in strength while dehydration takes place is perplexing.

This analogy is, of course, faulty because clay generally contains some carbonates, sulphates, and sulphides; whereas, this lime-silica body does not, or, if it does, they are present in mere traces. The opportunity for absorption of CO₂ in the process of manufacture should be borne in mind. It is possible that the drop in the curve from 600° to 750° is due to the expulsion of the small amount of CO₂ from the carbonate which is certain to be formed in the manufacture of the briquets. This explanation is substantiated by the work of Nauss, as reported by Bleining¹ whose conclusions are: "That, in regard to the decomposition of calcium carbonate, it is clearly shown that it begins to break up between 610° and 650° C, and before 700° is reached the evolution of carbon dioxide is going on quite rapidly." It is very probable that the CO₂ is completely expelled from the lime-silica body by the time 750° C is reached, and that from this temperature to higher ones, the bond is free to strengthen without other interruptions.

¹See bibliography, 31.

It is readily perceived that there are apparently two silicates formed, one between the temperatures 500° and 600° C, and the other forming at 850° , which continues up to $1,490^{\circ}$ C. It is also seen that the compound does not entirely lose its chemical bond after 400° C is past. These apparent facts suggest the possibility that the first silicate could be formed at 600° and, without burning to higher temperatures, used as a fireproof material. This hypothesis is advanced from the fact that after 400° C is past, this material does not completely lose its combining bond. Therefore this first silicate, upon being subjected to more heat, will strengthen itself indefinitely without bloating, fusing, or cracking, to which troubles the burnt clay wares used as fireproofing are subject. Doubtless the objection to the above will be advanced by some, that the well-known volume changes of silica at 800° will occur here, causing swelling and rupture of the material.¹ This is not the case, however, since the silica is in chemical combination with the lime and it has been proven that combined silica does not undergo volume changes when heated.¹

Some briquets composed of 20 per cent CaO, 80 per cent SiO_2 , to which was added 12 per cent of asbestos were fired in a test kiln to 1390° C. The effect of heat on this body was to decrease the tensile strength by eighty pounds per square inch. The broken briquets showed that the asbestos had fused, leaving the rest of the body intact. This will account for the decrease in some measure.

CARBONATE FILLER VERSUS SILICATE BOND.

To illustrate the difference in the strength of the carbonate filler and the silicate bond, briquets were made and, without hardening by steam, were allowed to age in the air for seven months. Table IX is a table of comparative results:

TABLE IX.

Per Cent CaO.	Per Cent SiO_2	Tensile strength after hardening in steam.	Tensile strength after hardening in air.
10.....	90	134	97
20.....	80	278	189
30.....	70	204	155
40.....	60	189	121
50.....	50	148	101

It is to be noticed from the above that the strength is not nearly so great in the case of the carbonate filler as it is with the silicate bond. However, by aging a longer period of time it is probable that the air hardened samples would become much stronger reaching the maximum in one and a half years.

¹See bibliography, 32.

THE EFFECT OF USING DOLOMITE AS A SUBSTITUTE FOR LIME.

To test the relative value of the silicate reaction, briquets were made of silica and dolomitic lime. The dolomitic lime was made by intimately mixing lime, CaO , and magnesia, MgO , in the ratio of one to one, which follows the mineralogical formula $\begin{matrix} \text{CaO} \\ \text{MgO} \end{matrix} \left\{ \begin{matrix} \\ \\ \end{matrix} \right. - 2\text{CO}_2$. The results are recorded in Table X.

TABLE X.

Per Cent Dolomite.	Per Cent SiO_2 .	Tensile strength.
10.....	90	116
20.....	80	232
30.....	70	168
40.....	60	158

In addition to the above tests, experiments were run on the effect of magnesia, MgO , and silica. See Table XI.

TABLE XI.

Per Cent MgO_2 .	Per cent SiO_2 .	Tensile strength.
10.....	90	92
20.....	85	186
30.....	80	132
40.....	75	124
45.....	70	112

It is readily seen from a study of these two tables that the magnesia reduces the tensile strength in a very marked manner. The reason for this is not clear, since MgO is almost as active as CaO in attacking SiO_2 ; so it can be inferred that the magnesium silicate formed is a much weaker bond than the calcium silicate.

SILICA AND ORTHOCLASE.

The suggestion was given that an attempt be made to chemically combine silica and feldspar by steam pressure. A series of tests was conducted in which the feldspar composed from 5 per cent up to 25 per cent of the total mixture. Another series was also run in which the silica formed from 5 per cent to 25 per cent of the composition. The steam pressure used was only a hundred pounds per square inch, which was all that could be obtained at that time. The tests were exposed for sixty hours to this pressure. Before putting into the autoclave, the briquets, although well dried, were apt to fall to pieces in handling. After exposure to the steam pressure they were equally fragile, showing that there had been no chemical reaction and that no bond had formed.

A SUBSTITUTE FOR CLAY-PRODUCTS.

In order to test the 20 per cent lime to 80 per cent silica mixture as a substitute for some of the clay products it was hand-pressed into a vase mold of plaster Paris. The vase dried safely and was hard enough when dried to handle and finish the joints. When hardened by steam it had, when struck with a pencil, the true hard ring of a vitrified clay biscuit. The material easily assumed and retained the shapes of the mold, hence it could be used as a terra cotta and also a stoneware body. It is not certain, at present, whether it could be cast thin enough for some of the thinner claywares or not. Small trials were also made by jiggering, which were very successful.

A great difficulty of the terra cotta and stoneware industries, which must be overcome, is the fact that, locally, the clay used, burns either red or buff. In order to glaze this with a pleasing effect, a pure white opaque enamel or "slip" is interposed between the glaze and the body. Needless to say this is a very expensive procedure, especially where tin-oxide is used as an opacifying agent. The pure white, fine-grained character of the lime-silica body will eliminate this great trouble of all the enameled clay industries. Another great point in its favor is the fact that it does not have to be burned. Stoneware is generally fired at cone 6, 1200° C, and terra cotta at cone 05, 1070° C. This, of course, represents a great expense for coal and also for kilns. Lime-silica is steamed at 150 pounds per square inch, and after the first cost of installation would require but little expense for maintenance of the hardening cylinder.

The material is strong enough and also sufficiently fire-resistant to be made into terra cotta, stoneware or enameled brick. The question as to whether it can be glazed or not was the next step in this investigation. There is no doubt¹ that it can be accomplished, since Dr. W. J. Michaelis Jr. has compounded a glaze for the regular sand-lime brick. This subject would constitute a great work by itself. It was suggested that Na₂O SiO₂ be applied as a glaze. This was done. The "water glass" when dried and hardened gave a good clear glaze but, as should be expected, was soluble in water, thus throwing it out of the field of commercial success.

CONCLUSIONS.

From the above work it is to be concluded that:

- (1) The best proportions of lime and silica to gain the highest tensile strength are 20 per cent of hydrated lime to 80 per cent of amorphous silica.
- (2) The best method tried, to improve the texture of the above composition is by means of molds made of plaster of Paris.
- (3) The tensile strength is greatly increased by the addition of mineral fibers, which have cohesion in themselves, like asbestos fiber.
- (4) The material is fire-proof² and can perhaps be used as a fire-proofing material.³
- (5) The effect is to decrease the tensile strength, when colloidal materials are introduced, like cement, clay, etc.

¹ Editor's note: Ceramists state that no satisfactory glaze has yet been discovered for such purposes.

² See bibliography, 18.

³ See bibliography, 9.

- (6) Steam pressure is absolutely essential.
- (7) The effect of using magnesia, MgO , either by itself or as dolomite, decreases the strength about one-third.
- (8) Silica and feldspar will not chemically combine at 100 pounds steam pressure.
- (9) The lime-silica mixture can be molded into shapes suitable for architectural decoration and also as substitutes for clay products, such as stoneware, enameled brick, and terra cotta.¹

BIBLIOGRAPHY.

The following list includes references indicated by number in footnotes of preceding pages.

- (1). Silica brickmaking. The industry in various countries.—Brick, October, 1903.
- (2). Sand-lime brick tests.—Technograph, No. 19, 1904 and 1905.
- (3). Sand-lime brick from brickmakers point of view.—Amer. Architect, April 16, 1904.
- (4). Sand-lime brick, Gerard-Meurer process.—Amer. Architect, August 1, 1903.
- (5). The Industry of Sand-stone bricks.—Revue Technique, Feb. 25, 1901.
- (6). Tests of Sand-lime and Concrete Building Blocks.—Eng. News, April 21, 1904.
- (7). Sand-lime bricks.—Jour. Chem. Met. and Min. Soc. of S. Africa, November, 1904.
- (8). Manufacture and Properties of Artificial Sandstone.—Trans-Amer. Ceramic Soc., 1902.
- (9). Tests of Strength and Fireproofing Qualities.—Eng. News, June 14, 1906.
- (10). Sand-lime brick, tests they have undergone.—Sci. Amer. Sup., August 25, 1906.
- (11). Sand-lime brick, manufacture and use.—Munic. Eng., Jan., 1907.
- (12). Sand-lime brick, petrographic work on.—Thon. Ind. Zeit. 25, p. 575 also 1660.
- (13). Artificial Sandstones or Sand-lime Brick.—Trans. Amer. Ceramic Soc., 1903.
- (14). Production of Lime and Sand-lime Brick in the U. S.—Mineral Resources of the U. S., 1906.
- (15). Comparative Study of Sand-lime and Clay Brick.—Clayworker, January, 1905.
- (16). The Chemistry of Sand-lime Brick.—Rock Products 7, 49.
- (17). Thonindustrie Zeitung, 1903, November 16, p. 193.
- (18). Thonindustrie Zeitung, Vol. 24, p. 1822.
- (19). Thonindustrie Zeitung, November 31, 1903.
- (20). Bulletin of the Wisconsin Survey, No. III, p. 399.
- (21). Thonindustrie Zeitung, Vol. 26, No. 104.
- (22). Thonindustrie Zeitung 32, (63), (77) also (80).
- (23). Bull. Soc. Encouragement, 1907, 1179-1201.
- (24). Thonindustrie Zeitung, 32, 1421, 1800.
- (25). Thonindustrie Zeitung, 32, 48, 573.
- (26). Thonindustrie Zeitung, 32, 54, 728.
- (27). Chem. Ftg. 32, 258.
- (28). Rock Products, 7, 47.
- (29). Bulletin No. 6, University of Illinois. Dept. of Ceramics.
- (30). U. S. Geol. Survey, 19th Ann. Report.
- (31). Ohio Geol. Survey Bull. No. 3, p. 175.
- (32). Journal of the American Chemical Soc., Feb., 1906, Shephard & Day.
- (33). Studies in the Formation of Silicates at Steam Temperatures.—T. R. Ernest, Thesis Univ. of Ill., 1908.

¹Editor's note: See note regarding glaze, p. 291. Silica is expensive.







UNIVERSITY OF ILLINOIS-URBANA



3 0112 086857189